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PHOSPHORUS Fertilizers FOR PULP PAPER

Progress Report on Work Performed in the Period October
to December 31, 1946, Under Contract A-10-C36-44-1518

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Chemical Research Division

PHOSPHORUS FILLINGS FOR MUNITIONS

Progress Report on Work Performed in the Period October 1
to December 31, 1946, Under Contract W-18-035-CWS-1318

By

J. C. Brosheer, F. A. Lenfesty, and P. L. Imes

Wilson Dam, Alabama

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PHOSPHORUS FILLINGS FOR MUNITIONS

Progress Report on Work Performed in the Period October 1

to December 31, 1946, Under Contract W-18-035-CISMS-1318

SUMMARY

Continuation of the study of phosphorus fillings for munitions under contract W-18-035-CISMS-1318 has included investigation of plastics that may be hardened at room temperature. Laboratory preparations of urea-formaldehyde, urea-furfural, furfural-formaldehyde, and furfural-benzaldehyde plastics have been made, and two commercial casting resins have been tested.

Preliminary small-scale firing tests have indicated that mixtures of hard plastics and granulated phosphorus have somewhat better burning characteristics than has elemental phosphorus alone. It was found, however, that the bursting charge is a critical factor in the performance of a phosphorus filling, and it is assumed that it will be necessary to procure or develop a suitable combination of burster and container to obtain the most satisfactory results with a given filling.

Further study of mixtures of each of several plastics with granulated phosphorus is planned. Methods for more exact evaluation of mixtures to be subjected to field firing tests are being considered.

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PHOSPHORUS FILLINGS FOR MUNITIONS

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Previous work on phosphorus fillings for munitions has shown that mixtures of granulated phosphorus and hardened plastics burn at satisfactory rates when ignited in the air. The work covered by the present report comprised a continuing search for suitable plastics, a further investigation to determine the optimum particle size of granulated phosphorus for the fillings, and preliminary firing tests for evaluation of experimental fillings.

PREPARATION OF CHARGES FOR FIRING TESTS

Charges for the exploratory firing tests consisted principally of granulated white phosphorus in synthetic resins and plaster of Paris. Two charges were prepared from phosphorus-sulfur compositions. Charges of massive white phosphorus served as controls. All the charges were retained in glass containers.

Materials

Urea-formaldehyde plastics may be prepared readily by dissolving urea in aqueous formaldehyde and adding an acid to accelerate solidification. The mole ratio of formaldehyde to urea may be varied from 1.5 to 2.5; increase of the ratio increases the time required for hardening of the acidified composition and decreases the hardness of the product. Such preparations shrink significantly on standing. Sulfuric acid was found to be a rapid accelerator and acetic acid a slow one. Citric acid proved to be less active than sulfuric acid but sufficiently rapid for use in the preparation of mixtures containing granulated phosphorus. The urea-formaldehyde resin used in the preparation of phosphorus fillings was prepared with 2 moles of formaldehyde, in 36 per cent aqueous solution, per mole of urea. The mixture was accelerated with 3 per cent, by weight, of powdered citric acid.

A condensed urea-formaldehyde resin was prepared by the method of Ripper (Ellis, Carleton. "The Chemistry of Synthetic Resins." Reinhold Publishing Corp., New York, 1936, p. 594). A mixture containing 2 moles of formaldehyde, as neutral 30 per cent solution, per mole of urea was refluxed for 10 hours with about 4 per cent of boric acid. The solution was then evaporated at 50° C. under a vacuum to form a thick sirup. The sirup solidified upon acidification, but more slowly than did the uncondensed reagents. The product was tougher, however, than that obtained from the uncondensed reagents. The condensed resin shrunk on standing, but it cracked much less than the corresponding uncondensed resin.

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Urea-furfural resins were prepared by dissolving 1 mole of urea in an equal weight of water, adding 1 mole of furfural, and acidifying the mixture with about 3 per cent, by weight, of citric acid. The product solidified but cracked badly when allowed to stand in the air.

Furfural and formaldehyde in a mole ratio of 1 to 1.6, upon acidification with concentrated hydrochloric acid, formed a resin that appeared to have satisfactory physical properties. A resin prepared similarly from furfural (1 mole) and benzaldehyde (1.6 moles) first appeared to have satisfactory properties, but it checked badly and disintegrated into relatively large pieces on standing about 5 weeks in the air. Both resins were very slow in setting at room temperature; several days were required to form a solid strong enough to be removed from the mold.

The commercial casting resins, Durcz 7421A, produced by Durez Plastics and Chemicals, Inc., and Duralon 30, produced by U. S. Stoneware Co., also were studied. Both resins formed hard, tough solids at room temperature when treated with the accelerators supplied by the manufacturers.

Plaster of Paris was prepared by heating gypsum. Casting plaster has been ordered.

Exploratory tests with wood flour and with short lengths of glass wool indicated that little, if any, advantage was obtained by the use of fillers in the plastics, and the investigation of fillers has been suspended.

Granulated phosphorus was prepared in a jet granulator in which molten phosphorus flowed by gravity through a glass tip into a vertical column of cold water that had been seeded with colloidal solid phosphorus by adding a small amount of a solution of phosphorus in alcohol. The seeding effects the marked supercooling characteristic of white phosphorus.

Attempts to prepare spheres of phosphorus 6 to 9 mm. in diameter were only partially successful. Although such spheres could be molded, the prospective results did not appear to warrant the time and effort that would be required to prepare the necessary mold. Phosphorus was cast in a sheet about 9 mm. thick, and the sheet was chiseled by hand into rough cubes. The cubes were placed in a ball mill with about twice their volume of 13 mm. silica pebbles and enough water to cover the mixture. After 8 hours of milling, the phosphorus particles were slightly rounded cubes. The process is unpromising.

Measurements of the weight of a known volume of granulated phosphorus, compacted by stirring, indicated that the interstitial spaces listed below were to be expected in the various forms of granulated phosphorus:

<u>Form of phosphorus</u>	<u>Interstitial space, %</u>
Jet granulated:	
2-mm. jet	45
1.3-mm. jet	39
0.8-mm. jet	34
Stirrer granulated	44
Ball-milled particles	
Approx. 2 mesh	36
Approx. 4 mesh	37
Cast cylinders of approx. equal diameter and height	42

Liquid autoptic phosphorus sulfide (80% P) was prepared by mixing molten phosphorus with lump sulfur. The phosphorus was a dark-colored product containing about 1 per cent of impurities. After standing for several days, the mixture was still heterogeneous, and filtration through a glass filter separated it into a liquid and a canary-yellow semisolid that was slightly rubbery and had the consistency of very soft putty. The puttylike material, which ignited as readily as elemental phosphorus and burned vigorously, was prepared for a firing test. Unfortunately, the burster failed, and the sample was lost. Attempts are being made to reproduce the puttylike material.

Filling the Containers

The containers for the solid charges were 150 ml. Pyrex beakers about 7.5 cm. high and 5.3 cm. in diameter. Burster wells were 7.5-cm. lengths of Pyrex tubing sealed at one end and of appropriate diameter to receive the burster.

In charging the beakers for firing tests, 135 ml. of granulated phosphorus was placed under water in the beaker, the water was siphoned off while a stream of carbon dioxide was directed onto the surface of the phosphorus, and sufficient liquid resin was added to fill the interstices in the phosphorus and provide a 5- to 10-mm. layer of straight plastic on top.

The burster well was inserted and the charge allowed to stand until the plastic set. Charges of massive phosphorus were prepared in the beakers by cooling to solidification 135 ml. of molten phosphorus with a burster well in place. The water covering the phosphorus was poured off and the phosphorus wiped dry and covered with a layer of plastic.

Containers for the liquid 80-20 phosphorus-sulfur eutectic were fabricated from glass tubing to approximate the size and shape of the 150-ml. beakers.

Beakers filled with massive phosphorus contained about 245 grams of phosphorus. Beakers filled with granulated phosphorus generally contained between 135 and 160 grams of phosphorus, depending upon the void space in the granulated phosphorus. By combining granulated phosphorus of different particle sizes to minimize the void space, mixtures containing 80 per cent phosphorus, by weight, or 210 grams per charge were prepared. The volume of the phosphorus filling in the beakers, incidentally, was about 60 per cent of the volume of filling that can be placed in the M15 grenade.

FIRING TESTS

In most of the firing tests the burster was a 5-cm. (2-inch) firecracker stemmed with a little moist earth. A slow fuse, prepared by soaking soft cotton cord in a strong solution of potassium nitrate and drying, was tied to the fuse of the firecracker and ignited. The method and materials proved to be safe, quite reliable, and sufficiently reproducible for use in exploratory firing tests.

In one series of tests, Primacord Bickford was used as the burster. The Primacord was inserted into an 8-mm. well, or suspended in an 18-mm. well, or packed into an 18-mm. well with four short lengths of Primacord. The Primacord was exploded with a No. 6 electric blasting cap. In a few tests No. 6 caps alone were used as unstemmed bursters in 18-mm. wells.

Tests of Various Plastic Compositions

In the first firing test of phosphorus-filled preparations, jet-granulated phosphorus (about 4 to 8 mesh) was mixed with various plastic compositions. The plastics were uncondensed urea-formaldehyde, condensed urea-formaldehyde, urea-furfural, and urea-furfural mixed with glass wool that had been cut in half-inch lengths. The preparations were exploded with firecrackers. Two containers filled with massive phosphorus were fired for comparison.

The individual shots were evaluated by observing the time of persistence of a screening smoke, the total time of burning, the maximum distance particles were thrown, and the size of the larger particles scattered by the explosion. The total time of burning was taken as the time in which individual particles continued to emit a fairly steady, although small, amount of smoke.

Slight pillar ing occurred on explosion of the straight phosphorus charges but not on explosion of the plastic-phosphorus charges. Because of the small amount of phosphorus in the charges, the persistence of a screening smoke in the variable, about 16 m.p.h., wind was considered to be relatively insignificant. The maximum distance particles were thrown by the explosion varied from 20 to 40 yards, but these data also are of little comparative value, for many pieces were thrown to heights of 15 to 20 yards. It was observed, however, that the straight phosphorus was fragmented into fine pieces and produced smoke for 1.5 to 2 minutes, whereas the plastic compositions each produced numerous particles 3/4 inch and more across that burned for 1.5 to 5 minutes. The best results, as measured by burning time and size of fragments, were obtained with a mixture containing condensed urea-formaldehyde resin which was so viscous that complete setting to a hard solid had not occurred at the time the charge was fired. Addition of glass wool filler to the urea-furfural mixture appeared to be detrimental, for the fragmentation was increased and the burning time decreased in comparison with the charge containing only urea-furfural and phosphorus.

The difficulty encountered in attempts to evaluate the several compositions in this series of firing tests indicated the need for a method of evaluation in which relative numerical values could be assigned to a test sample to express the results of the firing test. It was then assumed that a given sized fragment of a plastic-phosphorus composition would burn for a fairly definite time. It should be possible, therefore, to count the number of pieces burning at various predetermined times after the explosion of a test charge and thus obtain the number of pieces that burned for various lengths of time. The volume of each of these pieces would then be known, and the fragmentation of the charge could be estimated.

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6

A calibration curve was constructed from observations of the time of burning of cast cylinders, in which the height approximately equaled the diameter, of phosphorus and of urea-formaldehyde-phosphorus and urea-furfural-phosphorus mixtures. The cylinders were burned on a metal plate. Burning time was taken as the time during which a yellow flame of phosphorus persisted. A fairly smooth curve of burning time versus volume of material was obtained with the urea-furfural-phosphorus mixtures. Cylinders of phosphorus larger than 5 cc. (9 grams) burned completely within 3 to 4 minutes regardless of size, and results obtained with urea-formaldehyde-phosphorus samples were somewhat erratic. The results obtained with the urea-furfural mixture were smoothed to yield the following values.

<u>Burning time, min.</u>	<u>Volume, cc.</u>
1.0	0.3
1.5	0.7
2.0	1.6
2.5	2.7
3.0	4.0
4.0	7.6
5.0	11.7
6.0	15.8
7.0	20.0

Effect of Granule Size of Phosphorus in Urea-Furfural and Plaster of Paris Buses

Charges for the second series of firing tests comprised urea-furfural resin and granulated phosphorus of various particle sizes from 2 to 40 mesh. A few of the charges containing about 8-mesh phosphorus were divided by cardboard separators into either three short cylinders or four sectors.

The charges were burst with firecrackers, and the number of particles burning after various predetermined times was noted. Estimation of the fragmentation from the volume of the burning pieces proved of little significance, however, for the proportion of the total volume represented by the burning pieces generally was less than 10 per cent.

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In general, best results were obtained with small granules of phosphorus. The charges containing 40-mesh phosphorus were disrupted and thrown so much less violently by the burster that it was thought at first that the burster had been defective. Division of the filling into 3 short cylinders by cardboard separators appeared to be an improvement, but division of the cylindrical charge into sectors was without apparent advantage.

The plaster of Paris mixtures performed poorly in comparison with the urea-formaldehyde mixtures. In one of the plaster of Paris charges, however, the burster well was placed along the side of the container rather than in the center. This charge compared favorably with the best of the urea-furfural samples, and it was presumed that the strength and location of the bursting charge would be found to be a critical factor in the performance of mixtures of granulated phosphorus and plastic compositions.

Effect of Type of Burster

The third series of firing tests was made to determine the effect of high-explosive bursters on charges of massive phosphorus, liquid phosphorus sulfide eutectic, urea-furfural-granulated phosphorus mixtures, and plaster of Paris-granulated phosphorus mixtures. The high-explosive bursters were No. 6 electric blasting caps and Primacord Bickford. For comparison under the same atmospheric conditions, charges of massive phosphorus and of urea-furfural-granulated phosphorus were burst with firecrackers.

Although pillaring was marked in shots with the high-explosive bursters, the phosphorus sulfide was the only material that produced the mushroom type of pillar. Pillars obtained in other shots were of the relatively straight columnar type that is not so objectionable as the smoke-wasting mushroom type.

As was expected, the charges were scattered much less by the high-velocity caps and Primacord than by the firecrackers. The action of the fast bursters seemed to be largely that of a pulverizing burst that tossed the fragments up into the air and allowed them to fall back in the immediate vicinity of the explosion; roughly a quarter of the charge invariably remained in a pile at the site of the explosion. The urea-furfural and plaster of Paris mixtures showed more resistance to fragmentation than the massive phosphorus. Charges exploded with the high-explosive bursters burned about half as long as those exploded with firecrackers. It was apparent that even unstermed No. 6 caps were too brisant for the phosphorus mixtures.

One of the urea-furfural-granulated phosphorus preparations was burst with the powder from two firecrackers in an 8-mm. burster well. The burster was stemmed with moist earth. The shot resembled those obtained with high-velocity bursters more than those obtained with firecrackers. Even the firecrackers may be stronger than is necessary or desirable for charges in glass beakers.

One of the charges of straight phosphorus contained lengths of 8-mm. glass tubing, open at both ends, stucked parallel to the burster well, and filling as much as possible of the space occupied by the filling. The tubes were both surrounded by and filled with phosphorus. On explosion of the charge with a firecracker, many of the glass tubes were thrown as far as 25 yards without breaking, but they had little effect on the burning of the scattered charge.

Discussion of Results

Since all the firing tests were exploratory, more variables were uncovered than have been studied. The tests have indicated, however, that the best mixture that can be made from granulated phosphorus and a resin that sets up as a hard solid probably will contain fine particles of phosphorus. There has been indication also that a tacky, rubbery, or plastic mass may be better than a hard, brittle mass.

There is evidence that the characteristics of the bursting charge and perhaps the location of the burster in the body of the projectile will be critical factors in the performance of the filling under field conditions. An attempt will be made to obtain or fabricate a burster that will produce optimum performance of the experimental fillings.

The most pressing need is a quantitative method of evaluating the effect of the explosion of the burster on the experimental fillings. Since it appears that finely granulated phosphorus will produce the most satisfactory fillings, small-scale tests probably will give results that can be translated into predictions of field performance on a larger scale. Two methods of evaluation are under consideration. One is a measurement of the rate of burning of the exploded charge, and the other is a measurement of the fragmentation of the exploded charge.

The rate of burning might be measured by exploding the charge in a closed chamber through which a constant stream of air was flowing to an exhaust stack. Photoselectric measurement of the density of the fog in the stack should indicate the rate of burning. The apparatus could be calibrated by burning phosphorus at known rates while the standard gas flow was maintained through the chamber. Straight phosphorus exploded in such a chamber would be expected to evolve P_2O_5 at a high initial rate which would fall off rapidly. Desirable types of phosphorus fillings presumably would evolve P_2O_5 at a lower rate that would be maintained for a longer period of time.

The fragmentation probably could be measured easier than the rate of burning. Explosion of the charge in a spray chamber should permit subsequent determination of the size of the fragments.

Measurements made by either method probably could be used to estimate data that could be obtained by the other. Either method probably would permit more objective evaluation of the field performance of experimental fillings than does the present method of visual observation and timing of events that are broken up into a sequence of arbitrarily and indefinitely defined phenomena. Either method also would permit measurement under controlled conditions.

PLANS FOR FURTHER WORK

Mixtures of granulated phosphorus with several plastics, both laboratory products and commercial casting resins, are being prepared for additional exploratory firing tests.

M15 grenades will be filled with several of the mixtures that showed up best in the field firing tests with firecrackers as bursters. If the effect of the M6A4D fuzes supplied with the grenades simulates the effect of a high-velocity burster on charges in the small glass containers, attempts will be made to secure or prepare bursting charges for the grenades that will be more suitable for the experimental fillings.

Experimental fillings will be prepared with phosphorus sludge, a somewhat granulated, impure phosphorus obtained in relatively small quantities in the TVA phosphate plant.

Attempts will be made to obtain or prepare resins that set as tacky or puttylike masses, and such materials will be used in the preparation of experimental fillings.

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